

solid electrolyte interface

The Role of Electrolyte Upon the SEI Formation Characteristics and Low Temperature Performance of Lithium-Ion Cells with Graphite Anodes

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Abstract

Quarternary lithium-ion battery electrolyte solutions containing ester co-solvents in mixtures of carbonates have been demonstrated to have high conductivity at low temperatures ($< -20^{\circ}\text{C}$). However, in some cases the presence of such co-solvents does not directly translate into improved low temperature cell performance, presumably due to the formation of ionically resistive surface films on carbonaceous anodes. In order to understand this behavior, a number of lithium-graphite cells have been studied containing electrolytes with various ester co-solvents, including methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), and ethyl butyrate (EB). The charge/discharge characterization of these cells indicates that the higher molecular weight esters result in electrolytes which possess superior low temperature performance in contrast to the lower molecular weight ester-containing solutions, even though these solutions display lower conductivity values.

Introduction

Both NASA and the Air Force have interest in lithium-ion batteries with improved low temperature performance for a number of future applications. Under sponsorship by the Mars Exploration Program, we have focused upon developing advanced electrolyte systems with improved low temperature properties. This has led to the identification of a carbonate-based electrolyte, consisting of 1.0 M LiPF_6 in EC + DEC + DMC (33:33:34), that has been shown to have excellent performance at -20°C . (1,2) However, many applications, including future Mars Rovers, might be required to operate at temperatures as low as -40°C and high discharge rates (C/2). For this reason, we have investigated ethylene carbonate-based electrolytes to which appropriate co-solvents are added to sufficiently lower the viscosity and melting point of the solution. Similar approaches have been adopted using formates (i.e., methyl formate (MF)), acetates (i.e., MA, EA, and EP), as well as, other carbonates (i.e., ethyl methyl carbonate and methyl propyl carbonate) as co-solvents in lithium-ion electrolytes. (3-8) Most of these studies involving the use of

such solvents for Li-battery electrolyte formulations have consisted of binary (some ternary) solutions in which the low viscosity component is in large proportion (>30 vol%), magnifying any undesirable properties (i.e., film-formation characteristics).

In the present study, we have investigated a number of electrolyte solutions based on an optimized ternary mixture of carbonates (EC+DEC+DMC) to which potential co-solvents are added. The formulations studied include the following: 0.75M LiPF₆ in EC+DEC+DMC+X (1:1:1:1) (where x= methyl acetate (MA), ethyl acetate (EA), ethyl propionate (EP), ethyl butyrate (EB), methyl formate (MF), and ethyl methyl carbonate (EMC)). The selection of the electrolytes reported in this study is based upon the beneficial properties of adding low viscosity, low melting point solvent additives to base formulations of carbonate mixtures, which have been observed to have the desirable stability and passivating qualities. The use of multi-component quaternary solutions allows the physical properties of the electrolytes to be improved (higher conductivity and low freezing point), while still maintaining the desirable film-forming properties provided by mixtures of carbonates. The selection of the ester-based solvents is founded upon their favorable physical properties, as shown in Fig.1, and the demonstrated high conductivity when mixed into carbonate formulations. Although it has been determined that methyl acetate and ethyl acetate (lower molecular derivatives) form insulating films on the carbon electrodes preventing facile kinetics at low temperature, the higher molecular weight counterparts were studied with the expectation of decreased reactivity.

The electrolyte formulations were investigated in lithium-graphite (KS-44) half-cells, equipped with lithium reference electrode, to determine their compatibility with graphite electrodes. In addition to studying the charge/discharge characteristics of these cells at various temperatures, a.c. impedance and D.C. micropolarization techniques have been employed to probe the nature of the passive film-formation process. To augment these measurements, high resolution solid state ⁷Li NMR spectroscopy was used to investigate the solid electrolyte interface (SEI) formation in the graphite electrodes.(9) Specifically, the NMR method allows the direct quantitative determination of Li associated with the SEI as well as intercalated lithium. Some of the aspects that contribute to the formation of the SEI layer, its impact upon cell performance, and possible methods of characterization are illustrated in Fig. 2.

Results and Discussion

Conductivity Measurements

A number of carbonate-based electrolytes, containing low viscosity and low melting aliphatic ester additives, have been prepared and their conductivity measured over a temperature range of -60°C to 25°C. Of the electrolytes investigated, the formulations that displayed the highest conductivity at low temperatures (Fig. 1) were the ones containing the lower molecular weight esters. The conductivity varies with the following trend: 1.0M LiPF₆ EC + DEC + DMC + MA (1:1:1:1) > 1.0M LiPF₆ EC + DEC + DMC + EA (1:1:1:1) > 1.0M LiPF₆ EC + DEC + DMC + EP (1:1:1:1) > 1.0M LiPF₆ EC + DEC + DMC + EB (1:1:1:1).

Lithium-Graphite Half Cell Studies

A number of lithium-graphite cells were fabricated to study the viability of using these potential low temperature electrolytes. The use of these three electrode half-cells enables us to study the effect of different electrolytes upon the film formation characteristics on carbon electrodes (both graphite and MCMB-based materials). One purpose of these efforts is to determine the irreversible and reversible capacities of graphite electrodes in contact with various electrolyte solutions. The lithium-graphite half-cells also serve as an additional screening test to identify the compatibility and stability of candidate electrolytes with carbonaceous electrodes.

Charge/discharge characteristics

The nature of the electrolyte reactivity (and the concomitant SEI formation process) with lithiated carbon electrodes can be observed upon the first lithium intercalation process, as shown in Fig. 4. The electrolytes that display low irreversible capacity losses on the first cycle typically adopt potentials of Li intercalation more rapidly. In Fig. 5, the reversible capacities delivered after the fifth formation cycle of the cells are shown, with the EP-containing electrolyte resulting in the highest reversible capacity.

One aspect of studying the charge/discharge characteristics of the lithium metal-carbon half-cells included the assessment of the observed irreversible and reversible capacities as a function of electrolyte type. These results are summarized below in Table 1 in terms of mAh/g of active carbon used. When the group of acetate-containing electrolytes are considered (methyl acetate (MA)-, ethyl acetate (EA)-, ethyl propionate (EP)-, and ethyl butyrate (EB)-based electrolytes) a correlation is observed with the higher molecular weight additives resulting in higher reversible capacities after the fifth formation cycle. The cells displayed the following trend in increasing reversible capacity: EA (214.2 mAh/g) > MA (236.5 mAh/g) > EB (309.46 mAh/g) > EP (340.75 mAh/g). A similar type of trend was observed for the irreversible capacities, in that the higher molecular weight acetate-based electrolytes also tended to have higher irreversible capacities.

Electrolyte-Type	Rev.Cap mAh/g (1st Cycle)	Irr.Cap mAh/g (1st Cycle)	Rev.Cap mAh/g (5th Cycle)	Irr.Cap mAh/g (5th Cycle)
EC+DEC+DMC (1:1:1)	306.5	51.8	310.8	85.9
EC+DEC+DMC+MA (1:1:1:1)	201.5	36.9	236.5	56.9
EC+DEC+DMC+EA (1:1:1:1)	210.4	49.9	214.2	68.5
EC+DEC+DMC+EP (1:1:1:1)	233.4	49.06	340.75	88.30
EC+DEC+DMC+EB (1:1:1:1)	272.0	55.6	309.46	90.86

Table. 1. Reversible and irreversible capacities of graphite electrodes (Li-C cell) in contact with various electrolytes.

The charge/discharge characteristics of these cells were also investigated as a function of temperature at varying rates. In general, the cells containing the higher molecular weight acetate (EP and EB)-based electrolytes displayed superior performance

at low temperatures compared with the cells containing the lower molecular acetate (MA and EA)-based electrolytes, as shown in Fig. 6. The observed trends are understood as being related to the nature of the surface films formed on the carbon electrodes as the electrolyte type is varied. Although the MA- and EA-containing electrolytes result in cells with low irreversible capacities (which is usually suggestive of an electrolyte with good passivating characteristics) they display large polarization and charge transfer resistances. These conclusions are supported by linear (micro) and Tafel polarization studies that were conducted, although a detailed description of the data will be reported in a future publication. Thus, the kinetics of lithium intercalation and de-intercalation are not as facile due to the impervious nature of surface films of the MA- and EA-containing electrolytes in contrast to the EP and EB-containing cells. At -20°C , when the de-intercalation process was studied at a modest rate (25mA or $\sim \text{C}/12$) both the EB- and EP- electrolytes performed well ($> 2/3$ the room temperature capacity). As illustrated in Fig. 7, the EB-containing electrolyte resulted in cells which delivered $>90\%$ of the room temperature capacity at -20°C at a moderate rate ($\sim \text{C}/12$). Increased electrode polarization was observed at -20°C ($\sim 300\text{ mV}$), which is even larger for samples with high ionic film resistances (i.e., MA and EA containing electrolytes).

When the cells were discharged at low temperature (graphite intercalated with lithium), the capacity was significantly lower than that obtained when charging (de-intercalation), as shown in Fig. 8. Due to increased electrode polarization, the carbon electrode only adopts a potential $> 0.125\text{ V}$ vs Li^+/Li even though a potential of 0.025 V is applied to the cell, implying that lithium intercalation is not complete.

AC Impedance Measurements

In addition to studying the charge/discharge characteristics of these cells, a.c. impedance was used to probe the nature of the anode passivating film. Measurements were conducted for each cell after the formation process (5 cycles), as shown in Fig. 9. When the group of acetate containing cells is compared in terms of the charge transfer resistance, it was observed that the EB- and EP- containing cells displayed lower values than that observed with the lower molecular weight acetate derivatives.

AC impedance measurements were also taken at a number of temperatures (25, 0, -20 , and -40°C) to determine the impact of temperature upon the film resistance of the samples. It was generally observed that the film resistance dramatically increased upon going to lower temperatures. These results suggest that the nature of the SEI layer on the carbon electrode plays a large role, in addition to the bulk resistivity of the electrolyte, in determining the low temperature discharge performance. In terms of the ester-based electrolytes, the EP and EB-based electrolytes showed more favorable behavior at -20°C compared with the MA and EA-based solutions, displaying dramatically lower charge transfer resistances, as shown in Fig. 10.

AC impedance measurements were also performed on the cells after rate characterization tests (at various temperatures), as well as limited cycling at room temperature, to determine the stability of the electrolytes with cycling. This aspect is especially noteworthy, since the low temperature performance of lithium-ion cells

containing various low temperature electrolytes has been observed to degrade with cycling, implying that the SEI layer upon the carbon electrode becomes more resistive with prolonged operation. As shown in Fig. 11, the EB- and EP- containing cells displayed less of an increase in the R_B and R_{CT} values after cycling compared with the MA- and EA-containing electrolytes, shown in Fig. 12. These results suggest that the surface films are more inhibitive against further reaction in the case of the higher MW ester-based formulations compared to that of the lower MW ester-based solutions.

Conclusions

The results obtained from this study suggest that the nature of the SEI layer on the carbon electrode plays a large role in determining the low temperature discharge performance in addition to the ionic resistivity of the electrolyte in lithium-ion cells. Thus, in order to develop a lithium-ion cell capable of low temperature operation, it is necessary to identify an electrolyte which not only displays high conductivity, but also has favorable film formation characteristics at the carbon electrode. It was shown that lithium-graphite cells containing electrolytes possessing low molecular weight acetate co-solvents displayed much higher interfacial resistance values compared with the higher molecular weight acetate systems, such as solutions incorporating either ethyl butyrate or ethyl propionate.

References

1. M. C. Smart, C.-K. Huang, B.V. Ratnakumar, and S. Surampudi, *Proceedings of the Intersociety Energy Conversion Engineering Conference (IECEC)*, Honolulu, Hawaii, July, (1997).
2. M.C. Smart, B.V. Ratnakumar, C.-K. Huang, and S. Surampudi, *SAE Aerospace Power Systems Conference Proceedings*, P-322, p. 7-14 (1998).
3. A.H. Ohta, H. Koshina, H. Okuno, and H. Murai, *J. Power Sources*, **54**, 6 (1995).
4. D.E. Irish, Z. Deng and M. Odziemkowski, *J. Power Sources*, **54** (1), 28-33 (1995).
5. Y. Eineli, S.R. Thomas, R. Chadha, T.J. Blakley, and V.R. Koch, *J. Electrochem.Soc.*, **144** (3), 823-829 (1997).
6. Y. Ein-Eli, S.F. McDevitt, and R. Laura, *J. Electrochem. Soc.*, **145**, L1 (1998).
7. E.J. Plichta and W.K. Behl, *38th Power Sources Conference*, Cherry Hill, NJ, June 8-11, **1998**, 444.
8. M.C. Smart, C.-K. Huang, B.V. Ratnakumar, and S. Surampudi, *Proceedings, 37th Power Sources Conference*, pp. 239-242 (1996).
9. M.C. Smart, B.V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S.G. Greenbaum, A. Hightower, C.C. Ahn, and B. Fultz, "Irreversible capacities of graphite in low temperature electrolytes for lithium-ion batteries", submitted for publication.
10. Handbook of Chemistry and Physics, 64th Edition, CRC Press, Inc., Boca Raton, FL, 1984.

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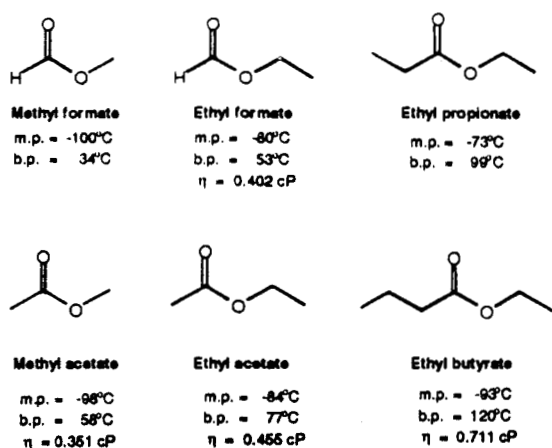


Fig. 1. Structures and properties of organic ester co-solvents. (10)

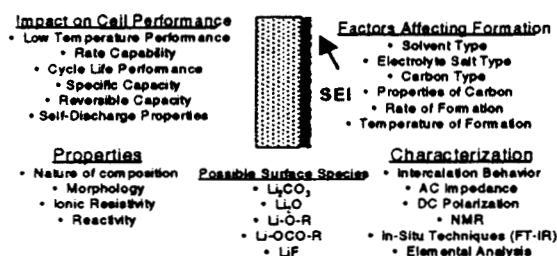


Fig. 2. The nature of the “solid electrolyte interface” (SEI) on carbon and its impact upon Li-Ion cell performance.

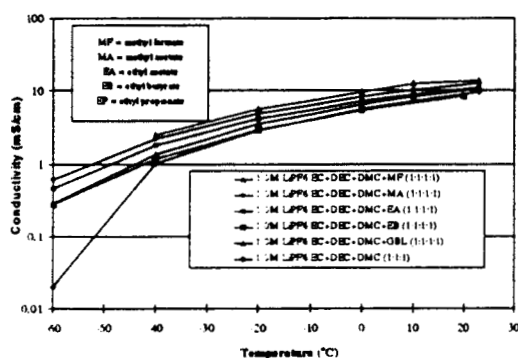


Fig. 3. Conductivity of Li ion battery electrolytes, based on solvent mixtures of EC, DEC, DMC, and aliphatic ester co-solvents.

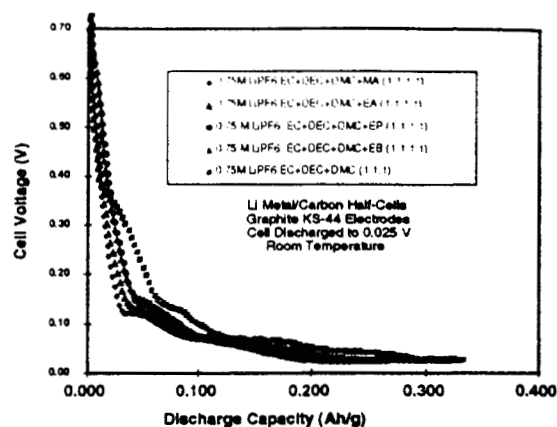


Fig. 4. First Li intercalation of graphite electrodes at room temperature in contact with different electrolytes.

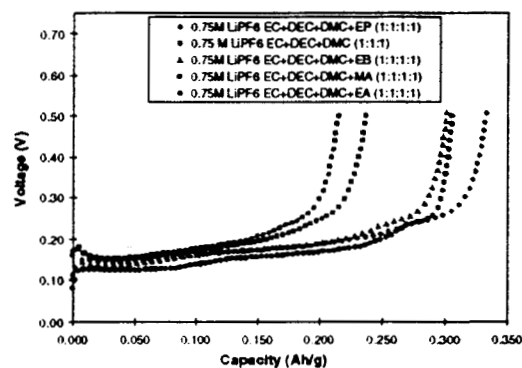


Fig. 5. Lithium de-Intercalation of graphite electrodes after fifth formation cycle.

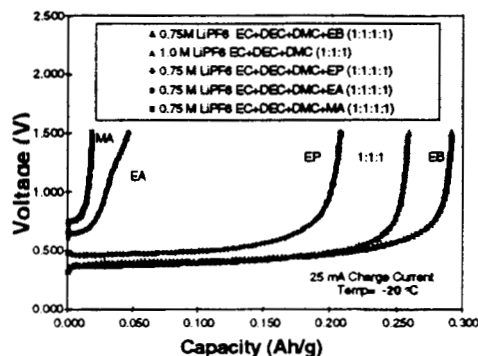


Fig. 6. Discharge curves of graphite electrodes in different electrolytes at low temperature (-20°C).

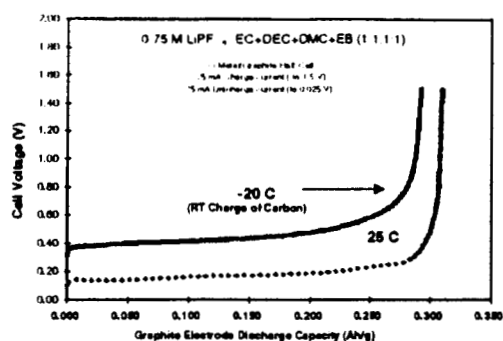


Fig. 7. Discharge curves of graphite electrode in contact with EB-containing electrolyte at different temperatures (25 and -20°C).

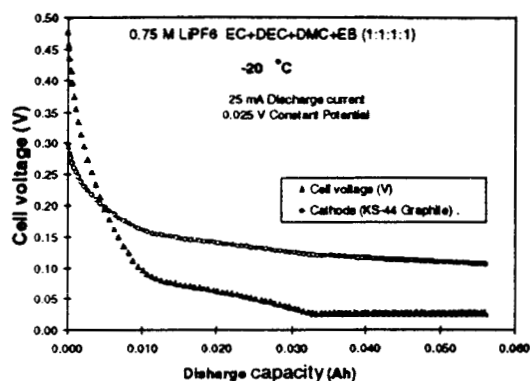


Fig.8. Charge curve of a graphite electrode in contact with an EB-containing electrolyte at low temperature (-20°C).

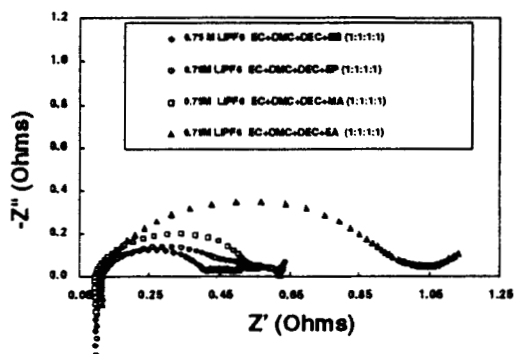


Fig.9. AC impedance (Nyquist) plots of lithium-graphite cells in contact with various electrolytes after formation cycles.

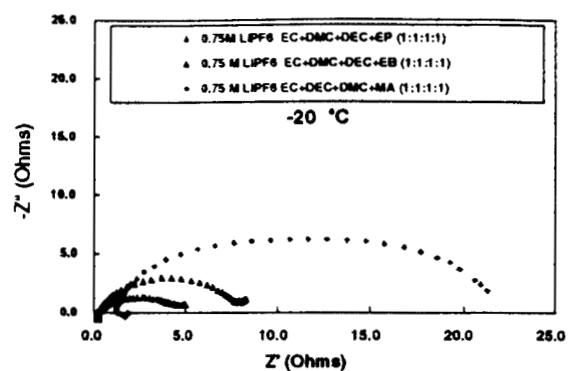


Fig.10. AC impedance (Nyquist) plots of lithium-graphite cells possessing ester-containing electrolytes at low temperature (-20°C).

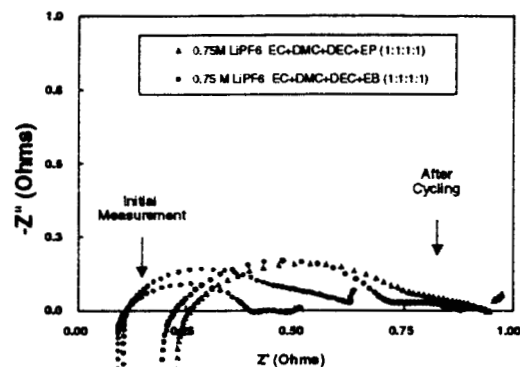


Fig. 11. AC impedance (Nyquist) plots of lithium-graphite cells possessing EP- and EB-containing electrolytes before and after cycling.

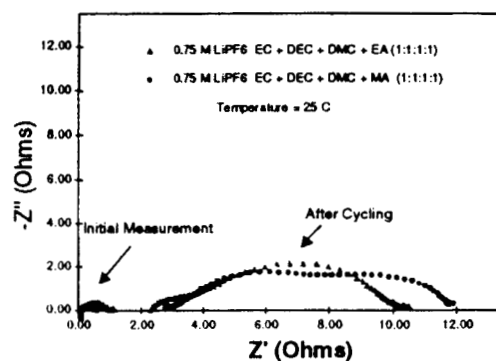


Fig. 12. AC impedance (Nyquist) plots of lithium-graphite cells possessing MA- and EA-containing electrolytes before and after cycling.